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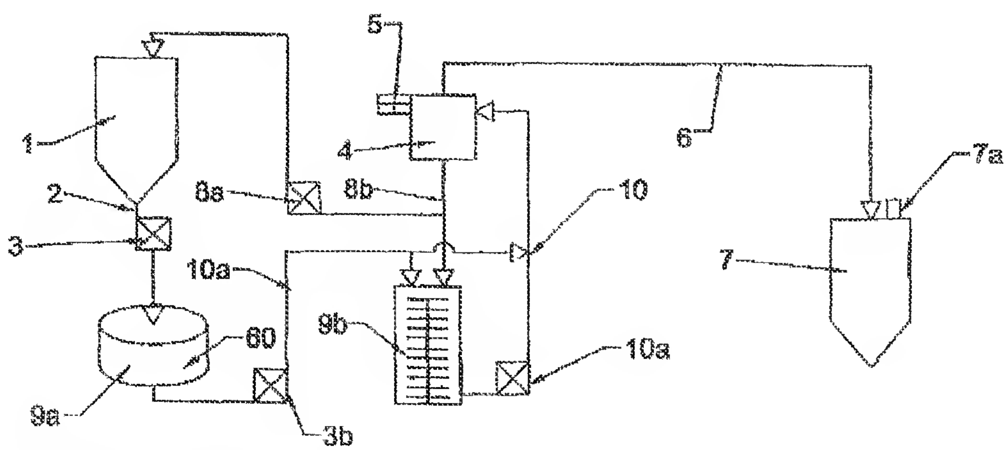
(54) Title: INCREASED REPLA CEMENT OF FLY ASH IN CEMENT COMPOSITIONS



(57) Abstract: Fly ash is subjected to a classification in which the classifier is adapted to create a centrifugal force sufficient to partition the fly ash into a particle size fraction with a mean particle size in the order of between 1 and 5 microns. A method and apparatus for particle 5size reduction of fly ash provides the pneumatic introduction of the fly ash into a mill which is either an impact mill or an injection mill or a combination thereof. The fly ash may be introduced pneumatically through injectors which are in opposed relationship and the resulting fractured and comminuted product is passed into an impact mill for further attrition.

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INCREASED REPLACEMENT OF FLY ASH IN CEMENT COMPOSITIONS

TECHNICAL FIELD OF THE INVENTION

This invention relates to cement compositions containing greater amounts of fly ash than hitherto with concomitant advantages in environmental control.

BACKGROUND ART

It is estimated that at present 30 to 40 million tons of fly ash are used as a partial replacement for Portland cement in concrete, resulting in the reduction of 20 to 30 million tons of CO_2 which would otherwise have been emitted by the production of an equivalent amount of Portland cement.

The increase in the replacement level of Portland cement with fly ash to a 35 percent level, say, would result in a corresponding decrease in about 310 million tons in the production of Portland cement which calculates at a decrease in CO_2 emissions of some 200 million tons. This would also result in a reduction in the mining of some 500 tons of limestone and clay.

Industrial standards generally require that fly ash conforms to certain specifications when used as a replacement material for Portland cement and these standards limit the extent to which fly ash can be used. This limit is attributable to its latent pozzolanic reactivity which results in the early strength development of the concrete being less than that of a corresponding concrete using Portland cement alone.

It is believed that the limits of latent pozzolanic reactivity of the fly ash is due to a limited surface area as the majority of the particles are spherical - including cenospheres and plurospheres.

It is therefore an object of the present invention to provide a method of increasing the surface area of the fly ash and to provide apparatus for carrying out this method.

Several methods of achieving this have been proposed, one of which includes the wet grinding of fly ash in a ball mill to cause particle size comminution. Another method involved the use of ultrasonic vibrations to cause deglommeration and to crack open the plurospheres and thus releasing encapsulated spheres.

DISCLOSURE OF THE INVENTION

According to the invention fly ash particulate material is subjected to a classification process in which the classifier is adapted to create a centrifugal force sufficient to partition the fly ash into a particle size fraction with a mean particle size in the order of about 1 to about 5 micron., and separating the undersized particles from the oversize particles

The centrifugal force may be generated by means of a rotor fan speed of at least 3000 r.p.m.

Such a material may be used as a replacement material to the order of 30 to 55 percent of Portland cement in concrete.

According further to the invention the oversize fraction is recycled for comminution to the same range, or disposed of.

In a preferred form of the invention the material is first processed in dry form in an impact mill and then in a pneumatic cyclone particle size classifier for separating the desired fraction from the oversize fraction. The oversize material may be continuously returned to the impact mill for comminution reprocessing while the desired product with a mean particle size of 1 to 5 microns is continuously conveyed to a storage silo.

A secondary impact mill may be added, if desired or required.

Should the fly ash contain water the recycled oversize material is mixed with the new wet fly ash and the mixture flash dried, thereby achieving an improvement in the efficiency of the feed rheology and therefore the drying efficiency and, secondly, for further comminution of the oversize fly ash material.

The product of the invention may be used as a replacement for Portland cement, or as a cementitious material for use in building products and materials, or as an additive, filler, extender or pigment in other industrial products.

In one form of the invention an impact mill is provided which has a vertically mounted shaft impeller with radial blades in an enclosed cylinder. The impeller is driven by a high speed motor mounted external to the cylinder. The fly ash material is fed to the impact mill pneumatically through high pressure air injectors which are located in opposed relationship and preferably at an angle of between 70 and 150 degrees above or below the horizontal depending on the desired airflow direction with such force that the imperfect spherical particles, such as plurospheres, cenospheres, agglomerated and oversize particles, are fractured thereby resulting in particles having an irregular shape and finer particle size, and therefore having a greater surface area.

The spaces between the outer edges of the blades and the inside surface of the cylinder should be reduced to a minimum otherwise the air used for moving the fly ash material through the mill will tend to escape without effecting the moving operation. Baffles or the like may be provided on the inside surface of the cylinder to overlap the free edges of the blades and thereby prevent a bypass movement of the air containing the fly ash material.

In another form of the invention, a mill is used which comprises a chamber with opposed pneumatic injection inlets to feed the fly ash material at elevated pressure to cause the particles to collide with such force that the imperfect spherical particles, such as plurospheres, cenospheres, agglomerated and oversize particles, are fractured thereby, resulting in particles having an irregular shape and finer particle size, and therefore having a greater surface area. As indicated above such a mill may be combined with the impact mill.

Examples

A particle size classification test was conducted, using previously accumulated data from test work, using a typical dry fly ash sample, to determine at which mean particle size the partitioning of fly ash material would equal or exceed the early strength development of concrete, when replacing Portland cement in a concrete mixture at a higher than normal replacement level of fly ash for Portland cement.

The fly ash sample material was mixed and split into separate samples of 50 kilograms each and marked for identification purposes as; FA1, FA2, and FA3. FA1 to be retained as the unprocessed fly ash sample material for comparative purposes. Particle size analysis of the unprocessed fly ash sample material determined the mean particle size of the sample at 12 micron and 90% of the material as being less than 44 micron.

A pneumatic double cyclone type separator, as typically used in the classification of fine particulate materials, was used as the classifier to effect partitioning at differing mean particle sizes. The rotor fan was typically fitted with a variable speed motor allowing for the control of rpm of the rotor fan and therefore the centrifugal force intensity of the cyclone, so as to be able to achieve different mean particle size partitioning at differing rpm.

Referring to Figure 1 of the drawings, there is shown diagrammatically a silo 1 from which the fly ash sample material is conveyed pneumatically by pump 3, via conduit 2, to a pneumatic cyclone 4, which is pneumatically energised by rotor fan 5. Samples FA2 and FA3 were independently processed being fed to the pneumatic cyclone 4 with rotor fan settings at 2500 rpm and 3100 rpm respectively; resulting in the undersize partitioned material fractions having means particle sizes of 5 micron and 2.9 micron respectively. The samples being independently collected in silo 7, via conduit 6. The partitioned oversize material is collected via conduit 8 and may be further processed for comminution as described below, or may be discarded.

The undersize partitioned material fractions of samples FA2 and FA3 were submitted for comparative compressive strength tests according to accepted standard testing

methods, together with the unprocessed fly ash sample material marked FA1, and a sample of the Portland cement, which was used in the cementitious mixtures of all the samples marked FA4. The results of the compressive strength tests are depicted in Table 1 below.

TABLE 1 - COMPRESSIVE STRENGTH - MEAN PARTICLE SIZE - COMPARISONS

SAMPLE - identification	FA 1	FA 2	FA 3	FA 4
CONCRETE MIX INGREDIENTS	kilos	kilos	kilos	kilos
Coarse and fine aggregates	1 839	1 839	1 839	1 839
Portland cement	201	201	201	310
Fly ash	109	109	109	0
water	201	201	201	201
TOTAL - weight per cubic metre	2 350	2 350	2 350	2 350
Compressive strength - 28 days - N/m²	34	38	44	42
Mean Particle Size* FA - micron	12	5	2.9	0
Mean Particle Size* PC - micron	12	12	12	12
Water / Cement ratio	0.65	0.65	0.65	0.65
PC / FA ratio percent	65/35	65/35	65/35	100/0

NOTES:

Kilos = kilogram

N/m^2 = Newtons per square metre

FA = Fly Ash

PC = Portland Cement

Micron= Micrometres

EXAMPLE 1

Referring to Figure 2 of the drawings, there is shown diagrammatically dry fly ash material being pneumatically conveyed by pneumatic pump 3, from silo 1, via conduit 2, to impact mill 9. Pneumatic Pump 3, being a high pressure type compressor, controls the feed of fly ash through impact mills 9, 11, and 12, as diagrammatically shown in Figures 2, 3, and 4. Impact mills 9, 11, and 12, as diagrammatically shown in Figures 2, 3, and 4, are of the type as having a vertically mounted impeller, having a plurality of tangentially attached blades, in an enclosed cylindrical vessel. The impeller is driven by a high speed motor mounted external to the vessel. The high speed motor is geared to generate rpm of between

1400 to 4000, and, depending on the dimensions and throughput capacity of the cylindrical vessel, may be 1o to 50 horse power. Typically throughput of 10 tonne per hour will require a 30 horse power motor to maintain a 3000 rpm impeller speed.

Processed material from impact mill 9, is pneumatically conveyed by pump 10a, to pneumatic cyclone 4 for partitioning as described in example 5. The oversize coarse partitioned material is returned to impact mill 11 via conduit 8 or is returned to silo 1 via conduit 8a and pneumatic pump 8 for reprocessing. The undersize desired fly ash material, is conveyed to product storage silo 7a. Exhaust air is dispersed through bag house 7a.

The oversize particles may be returned to the mill 9 or returned to the silo 1 via pump 8a.

EXAMPLE 2

Referring to Figure 3 of the drawings, there is shown diagrammatically dry fly ash material being fed from silo 1, by pneumatic pump 3, via conduit 2, to a primary impart mill 9, for size comminution as described in Figure 2, and, in series, a secondary impact mill 11, which is fed by pump 13a via conduit 13, material primarily comminuted in impact mill 9, for further comminution processing.

Processed material from impact mill 11, is pneumatically conveyed by pump 10a, via conduit 10, to pneumatic cyclone 4, for partitioning as described above with reference to Figure 1. The oversize coarse partitioned material is returned to impact mill 11, via conduit 8b, by pneumatic pump, to silo 1, for further comminution processing, or may be returned to impact mill 9, via conduit 8a, for further comminution processing, depending on the particle size comminution desired. The predetermined desired undersize material, having a mean particle size of between 1 to 5 micron, is conveyed, via conduit 6, under the influence of gravity and the cyclone air stream, to silo 7.

EXAMPLE 3

The invention also provides a method for the blending of recycled partitioned oversize dry fly ash material with wet fly ash material, which is in the state of vacuumed filter cake, produced as a result of having been dewatered subsequent to a hydrometallurgical process, or, subsequent to recovery from a landfill lagoon. Generally fly ash filter cake material will contain residual moisture of between 13% to 17%, and in order to be suitable as a feed material to a flash drying unit requires a residual moisture content of the feed material to be 10% or less.

Referring to Figure 4 of the drawings, there is shown diagrammatically fly ash filter cake material being fed by a conveyor 14, to hopper 15 and oversize coarse dry fly ash material, which has been partitioned in pneumatic cyclone 4, being pneumatically conveyed by pump 22, via conduit 23, for blending with the wet fly ash filter cake material in pug mill 16. The recycled oversize dry fly ash material required to obtain a suitable blended material for efficient feed to a flash drying unit is found to be 45% to 55% by weight of that of the vacuumed filter cake material.

The blended recycled dry fly ash material and the wet filter cake fly ash material is fed by screw conveyor 17 to flash dryer 19. The flue gas stream created by burner 18, conveys the dried fly ash material via flue conduit 20, to thermally protected impact mill 12, which is fitted with bag house 21, for release of excess gases.

Dried fly ash material is processed for particle comminution in impact mill 12, as previously described in EXAMPLE 1, and is simultaneously cooled. The cooled material is pneumatically conveyed by pump 13a, via conduit 13, from impact mill 12, to impact mill 11 for further comminution, or, may be conveyed directly to pneumatic cyclone 4, by pump 13a, via conduit 24, depending on the extent of the comminution required.

Fly ash material conveyed by pumps 13a or 10a to pneumatic cyclone size classifier 4, via conduits 24 or 10, is partitioned to the desired undersize mean particle size and

conveyed to silo 7 for storage. The oversize coarse fly ash material is conveyed to pug mill 16, by pneumatic pump 22, via conduit 23, as previously described, or may be split in a manifold (not diagrammatically shown), whereby a portion of the material may recycled to the pug mill 16, via conduit 23, the other portion being returned to impact mill 11 for comminution reprocessing, via conduit 23a.

EXAMPLE 4

Referring to Figures 5, 5a and 5b, the impact mill is a blast chamber shown in Figures 5a as an octagonal chamber with a plurality of injection nozzles 60 through which the fly ash is introduced from the silo at high pressure by means of high pressure compressor 103.

The nozzles are mounted in opposition so that the introduced fly ash collides head-on resulting in the fracture of the spherical particles.

The nozzles may have diameters of from 6 to 13 mm depending on the throughput design. Typically a 13 mm nozzle with an air flow rate of 330 to 340 cubic ft/min (cfm) will generate 7 bar pressure which, through a 32 mm conduit will provide a feed rate of 900 to 1000 Kg of fly ash per hour.

In Figure 5 the impact mill 9b is shown, as described above. This impact mill may be fed from the exhaust outlet of the blast chamber 9a , or directly from the compressor 3, through injector nozzles 60.

Material processed in blast chamber 9a, as shown in Figure 5, is pneumatically conveyed by compressor pump 3b via conduit 10a and 10, directly to pneumatic cyclone 4. The classified desired undersize fly ash material, having a means particle size of between 1 to 5 micron, but preferably of 2.5 micron, is conveyed, via conduit 6, to silo 7. The oversize coarse partitioned material is conveyed and returned via conduit 8a, to silo 1, for further comminution, or, material processed in blast chamber 9a, is conveyed to impact mill 9b, for additional comminution and subsequently conveyed via conduit 10 by pneumatic

pump 10a to pneumatic cyclone 4 for classification. The undersize coarse material being returned to silo 1, or to impact mill 9b, for further comminution. The desired undersize fly ash material, is conveyed to product storage silo 7a. Exhaust air is dispersed through bag house 7a.

CLAIMS:

1. A method of pneumatically classifying fly ash including the step of subjecting it to a classification process, characterised in that
the classifier is adapted to create a centrifugal force sufficient to partition the fly ash into an undersize fraction with a mean particle size in the order of between 1 and 5 microns, and into the resultant oversize fraction.

2. The method as claimed in claim 1 characterised in that the centrifugal force is pneumatically created by a rotor fan speed of at least 3000 r.p.m.

3. The method as claimed in either claim 1 or claim 2 characterised in that the fly ash is first pneumatically conveyed through a high speed impact mill at velocities sufficient to cause impacting of particles with the high speed revolving impeller blades to cause resultant fracturing and comminution.

4. The method as claimed in claim 1 or claim 2 characterised in that the fly ash is pneumatically conveyed through opposed nozzles into a mill at velocities sufficient to cause autogenous impacting of the particles and resultant fracturing and comminution.

5. The method as claimed in either of claim 3 or 4 characterised in that the pneumatically classified oversize partitioned material is continuously recycled to the mill for additional comminution and the desired underside partitioned fraction is conveyed to a silo for storage.

6. The method as claimed in any of claims 3 to 5 characterised in that dried material exiting a drier, such as a flash drier, is pneumatically classified and the partitioned oversize material is recycled and is back-mixed with the new wet fly ash as feed material to the drier.

7. A method according to any of claims 3 to 6 characterised in that the same airflow, required to effect the desired comminution results, is used to convey the processed material from the mill to a pneumatic classifier and to be of sufficient pneumatic velocity to cause partitioning of desired undersize from oversize material.

8. Apparatus for carrying out the method of claims 3 to 7 including an impact mill characterised in that the mill has a vertically mounted shaft impeller with radial blades, driven by an external high speed motor, air injector nozzles for high pressure fly ash injection located in opposed relationship and adapted first to cause pneumatically accelerated particles to collide with themselves and subsequently, being conveyed in the same air-stream, with the high speed rotating impeller blades with such force that the imperfect spherical particles are fractured and comminuted to an irregular shape and finer particle size of less than 5 micron thus having a much greater surface area per unit volume.

9. Apparatus as claimed in claim 8 characterised in that the mill has air injectors for fly ash located in opposed relationship, positioned at an angle of between 70° to 150° above or below the horizontal depending on the desired airflow direction, and adapted to cause the particles to collide with themselves.

10 The apparatus as claimed in claims 8 or 9 characterised in that the spaces between the outer edges of the blades and the inside surface of the mill is minimal and that baffles are provided on the inside of the mill to overlap the free edges of the blades to prevent bypass of air containing fly ash.

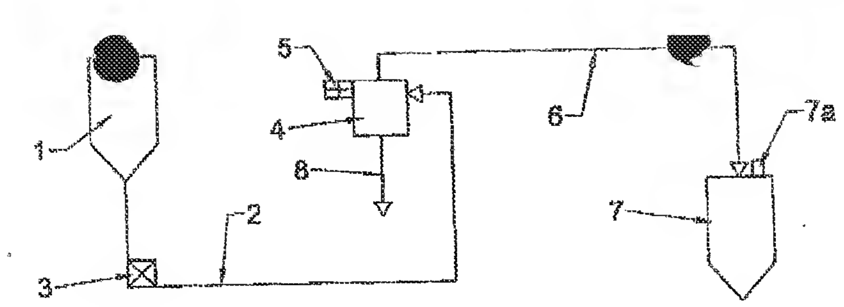

FIGURE 1

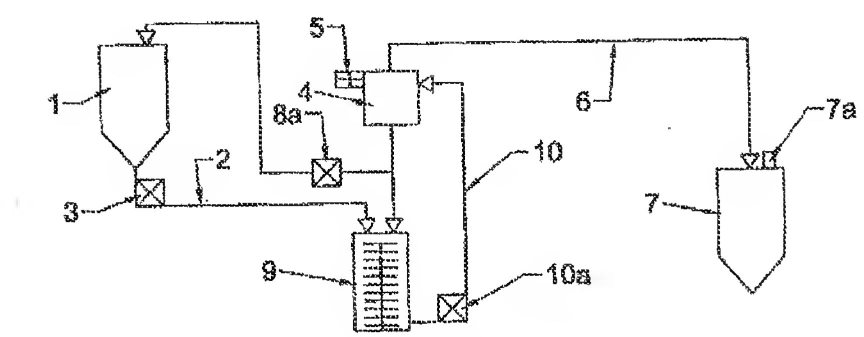

FIGURE 2

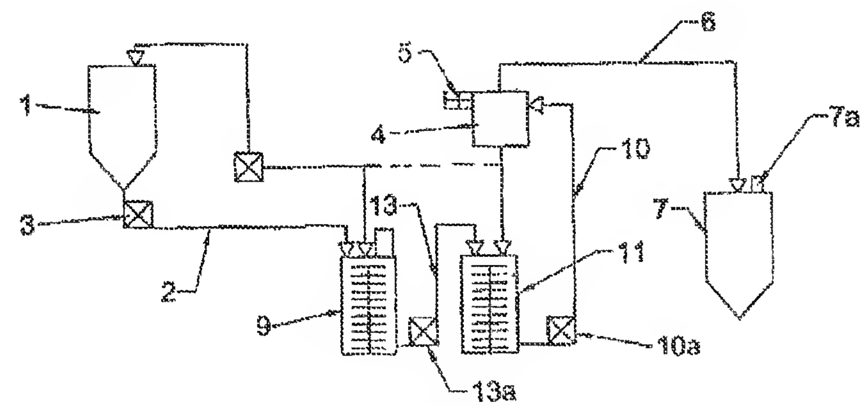

FIGURE 3

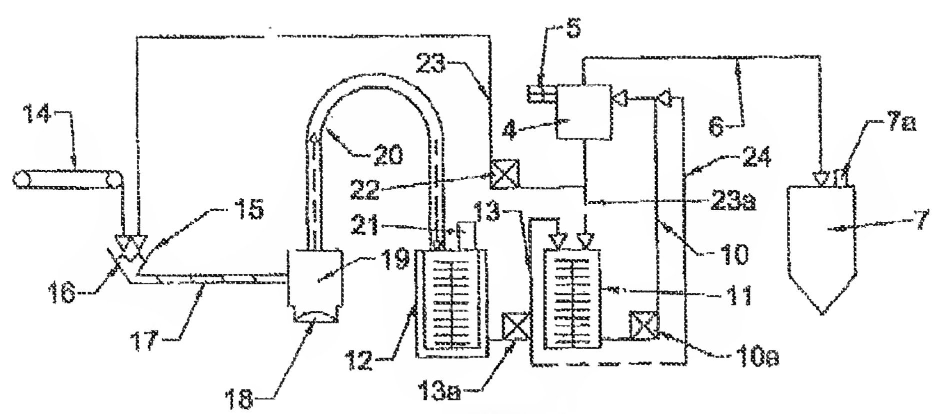

FIGURE 4

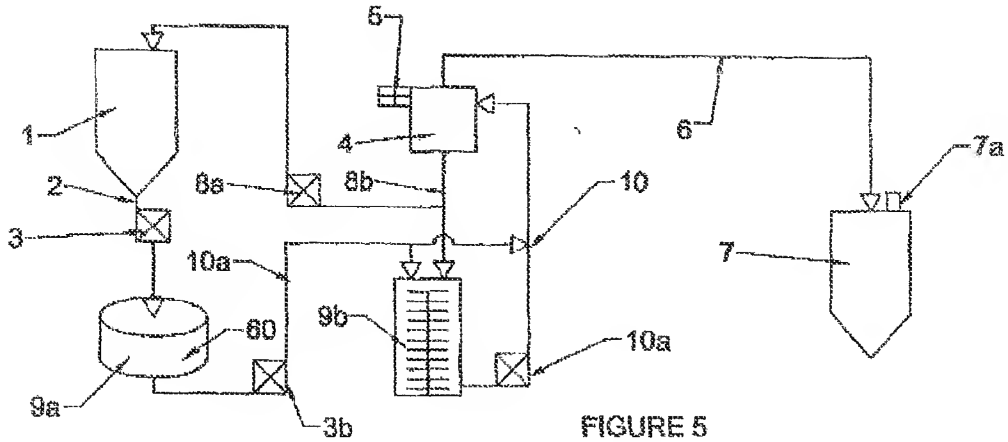

FIGURE 5

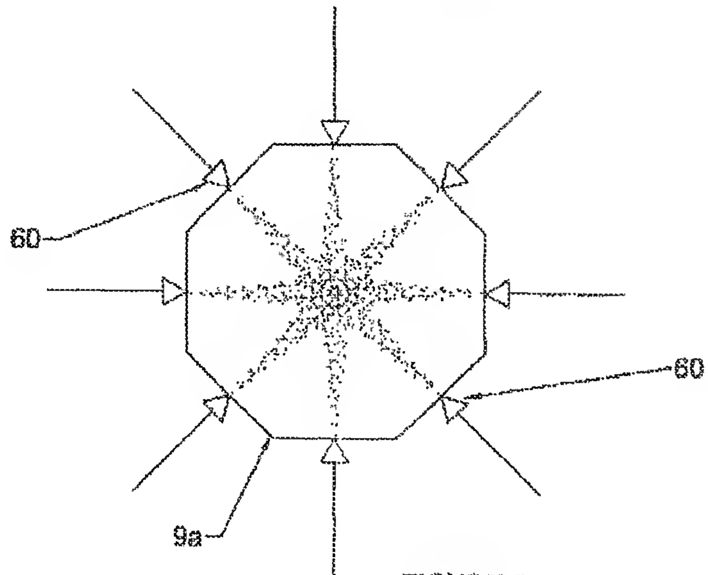

FIGURE 5a

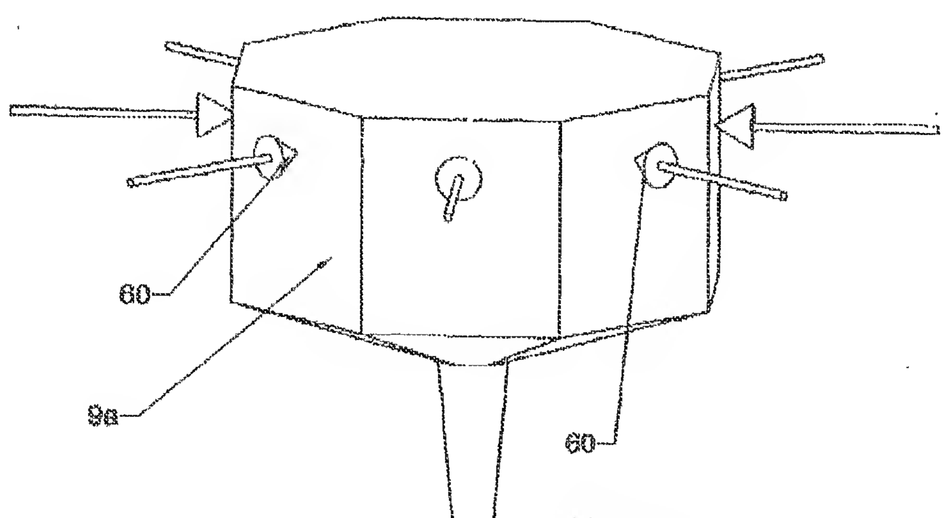

FIGURE 5b

INTERNATIONAL SEARCH REPORT

PCT/ZA2004/000009

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C04B18/08 B02C19/06 B02C13/14 B03B9/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C04B B02C B03B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 853 475 A (JATURAPITAKKUL CHAI ET AL) 29 December 1998 (1998-12-29) the whole document	1
Y	US 3 224 686 A (WALLACE JR CURTIS C) 21 December 1965 (1965-12-21) the whole document	8
X	US 6 038 987 A (KOSHINSKI CASMIR J) 21 March 2000 (2000-03-21) the whole document	1-5,7-9
X	US 6 269 952 B1 (WATT JOHN H ET AL) 7 August 2001 (2001-08-07)	1,4,5
A	the whole document	8

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
18 June 2004	02/07/2004

Name and mailing address of the ISA	Authorized officer
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2 932 458 A (CROFT GEORGE M ET AL) 12 April 1960 (1960-04-12) the whole document	5
A	US 4 698 289 A (EARL GEOFFREY H ET AL) 6 October 1987 (1987-10-06) the whole document	6
Y	US 4 504 017 A (ANDREWS NORWOOD H) 12 March 1985 (1985-03-12) the whole document	8
Y	US 4 087 052 A (ROHRBACH DECEASED HANS) 2 May 1978 (1978-05-02) the whole document	8

INTERNATIONAL SEARCH REPORT

Information on patent family members

PCT/ZA2004/000009

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 5853475	A	29-12-1998	US	5624491 A	29-04-1997
			AU	2639495 A	18-12-1995
			CA	2190729 A1	30-11-1995
			EP	0760949 A1	12-03-1997
			EP	0978723 A2	09-02-2000
			JP	10504641 T	06-05-1998
			WO	9532423 A2	30-11-1995
US 3224686	A	21-12-1965	BE	631610 A	
			CH	400733 A	15-10-1965
			DE	1291604 B	27-03-1969
			FR	1355213 A	13-03-1964
			GB	958484 A	21-05-1964
US 6038987	A	21-03-2000	AU	2219300 A	01-08-2000
			CA	2358494 A1	20-07-2000
			EP	1328759 A2	23-07-2003
			WO	0042357 A2	20-07-2000
US 6269952	B1	07-08-2001	AT	215403 T	15-04-2002
			AU	7845698 A	03-07-1998
			DE	69711692 D1	08-05-2002
			DE	69711692 T2	28-11-2002
			EP	0948410 A1	13-10-1999
			ES	2175491 T3	16-11-2002
			WO	9825704 A1	18-06-1998
			GB	2320245 A ,B	17-06-1998
			PT	948410 T	30-09-2002
US 2932458	A	12-04-1960	NONE		
US 4698289	A	06-10-1987	US	4592988 A	03-06-1986
			AU	4725985 A	07-03-1986
			BR	8506878 A	09-12-1986
			EP	0198839 A1	29-10-1986
			JP	62500054 T	08-01-1987
			WO	8601314 A1	27-02-1986
US 4504017	A	12-03-1985	NONE		
US 4087052	A	02-05-1978	DE	2428626 A1	09-09-1976